

Electrochemical performance of lead acid battery using ammonium hydrogen sulphate with different alkyl groups

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Abstract In this work, the application of ionic liquids (ILs)—mono-, bicyclohexyl, monohexyl and tetrahexyl ammonium hydrogen sulphate—as electrolyte additives on the electrochemical performance of lead acid batteries is proposed. The electrochemical behaviour of Pb–1.66% Sb–0.24% Sn alloy in sulphuric acid solution is investigated in the presence of the mentioned ILs with different numbers of alkyl or cycloalkyl chains. Particularly, the hydrogen and oxygen evolution potential and anodic layer characteristics were studied using cyclic and linear sweep voltammetric methods. The obtained results indicate that hydrogen evolution overpotential of Pb/Sb/Sn alloy in the presence of ILs increases. This overpotential mainly depends on the concentration of ILs and the number of alkyl and cycloalkyl chains on the cations. Also, the difference between the oxygen oxidation potential in anodic and cathodic scans (ΔE) decreases using different ILs.

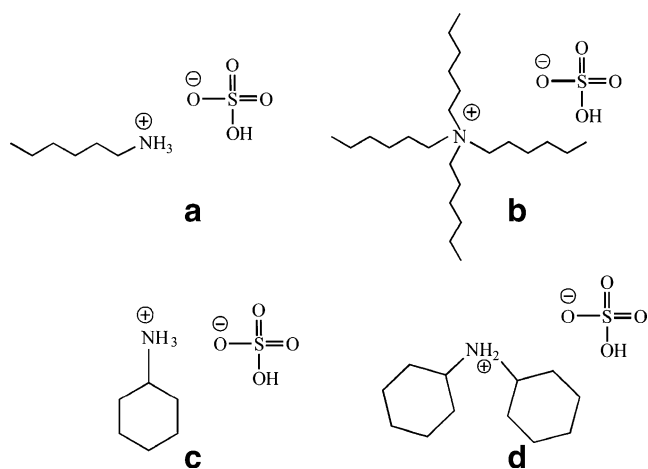
Keywords Lead acid battery · Ionic liquids · Cyclic voltammetry · Lead–antimony alloy · Alkyl ammonium hydrogen sulphate

Introduction

Lead acid battery is mainly still widely used as a starter source in the automotive field, although it has a growing number of other applications. It has some important advantages such as, low cost, high voltage per cell, and good capacity and cycle life [1, 2]. One of the main

problems in these batteries is water loss. Water loss is an ageing factor that cannot be compensated by refilling [3]. When lead acid batteries are charged or discharged, water is oxidized or reduced to oxygen and hydrogen gas, respectively. Therefore, the need of frequent maintenance increases corrosion and decreases lifetime. The grid's alloy components (lead alloys), which are used in lead acid battery electrodes, play a very important role on their electrochemical performance, mainly on the overpotential of oxygen and hydrogen evolutions. Electrolyte composition and additives are other important parameters which affect the overpotential of water decomposition. Therefore, plenty of studies are reported on the effect of some material additives in the lead alloy grids, such as Sb, Ca and Se [4–6], and of using of H_3PO_4 and other electrolyte additives on the performance of lead acid batteries [7]. Although antimony is the most popular additive in lead alloy grids, it mainly decreases the overpotential of hydrogen evolution at the negative plate. Also, antimony causes early decomposition of water and increases the self-discharge in a battery [8, 9]. There are some reports about useful additives to improve cycle life and self-discharge and to increase the oxygen overpotential on the positive electrode [10–12]. Ionic liquids (ILs), which have been widely promoted as 'green solvents', are attracting much attention for applications in many fields of chemistry and industry due to their chemical and thermal stability, wide electrochemical windows, low vapour pressure and high ionic conductivity properties [13–15]. Nowadays, ILs are being considered as a novel liquid or additive for electrolyte of electrochemical devices such as fuel cell [16], solar cell [17] and high-energy density batteries [18, 19]. In this work, we studied the effect of organic groups (alkyl and cycloalkyl) of ammonium hydrogen sulphate ionic liquids with the same anion (Scheme 1) on the potential windows of water

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Scheme 1 Molecular structure of hexyl ammonium hydrogen sulphate (**a**), tetrahexyl ammonium hydrogen sulphate (**b**), cyclohexyl ammonium hydrogen sulphate (**c**) and bicyclohexyl ammonium hydrogen sulphate (**d**)

decomposition and electrochemical behaviour of lead antimony alloy and paste in sulphuric acid. All of the ionic liquids in this study are stable in the sulphuric acid and potential range from -2.5 to $+2.5$ V.

Experimental

Apparatus

All voltammetric experiments were performed using SAMA 500 Electroanalyzer System, (Isfahan, Iran) connected to a personal computer. For all experiments, a conventional three-electrode system was used which consisted of a working electrode (Pb–Sb–Sn alloy or carbon–lead oxide paste electrode), a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

Materials and reagents

Analytical reagent grade chemicals and doubly distilled water were used in the preparation of all solutions. Graphite powder and lead oxide powder from Merck (Darmstadt, Germany) and high-viscosity paraffin oil from Fluka (Taufkirchen, Germany) were used for the preparation of lead oxide–carbon paste electrode. The electrolyte was 4.0 mol dm^{-3} sulphuric acid which was prepared from concentrated H_2SO_4 (Merck) and doubly distilled water. Ionic liquids (hexyl, monocyclohexyl, bicyclohexyl ammonium hydrogen sulphate) employed in this study were synthesized and purified in our laboratory using the recommended method in [20] and tetrahexyl ammonium hydrogen sulphate purchased from Sigma-Aldrich (Switzerland). For the synthesis of ILs, hexyl

amine (Merk), dichloromethane (Merk), *n*-hexan (Merk), monocyclohexyl amine and bicyclohexyl amine (Sigma-Aldrich) were applied. Ionic liquids solutions (5.0 , 10.0 , 15.0 and $20.0 \text{ } \mu\text{g ml}^{-1}$) were prepared by adding an appropriate amount of ILs to 4.0 mol dm^{-3} sulphuric acid.

Synthesis of acidic ionic liquid

Synthesis of HAHS Firstly, hexyl amine (2.5 ml , 20 mmol) was dissolved in dichloromethane (10 ml) and then 1 ml of concentrated H_2SO_4 (20 mmol) was added slowly at 0°C . The reaction mixture was stirred at room temperature for 30 min . The resulting ionic liquid was washed by *n*-hexan and dried in a vacuum at 80°C . The other ILs, such as monocyclohexyl ammonium hydrogen sulphate (MCHAHS) and bicyclohexyl ammonium hydrogen sulphate (BCHAHS), had been synthesised in the same way using 20 mmol bicyclohexyl amine and sulphuric acid. Figure 1a–c shows the IR (KBr) and ^1H NMR (400 MHz , D_2O) spectra of hexyl ammonium hydrogen sulphate (HAHS), MCHAHS and BCHAHS, respectively.

The IR spectra show clearly: 3450 cm^{-1} (N–H stretching), 2950 cm^{-1} (C–H stretching), 1640 cm^{-1} (N–H bending), 1170 cm^{-1} (S=O stretching) and 585 cm^{-1} (S–O stretching).

^1H NMR of HAHS: 0.746 triplet CH_2 (a), 1.2 multiplet CH_2 (b,c), 1.5 multiplet CH_2 (d), 2.8 triplet CH_2 (e), 7.3 triplet NH_3 (f) and 4.7 DOH (h).

^1H NMR of MCHAHS: 1 and 1.2 multiplet CH_2 (a), 1.5 , 1.6 and 1.8 multiplet CH_2 (b), 3.02 CH_2 (c), 7.5 triplet NH_3 (d) and 4.7 DOH (f).

^1H -NMR of BCHAHS: 1 and 1.2 CH_2 (a), 1.5 , 1.7 and 1.9 multiplet CH_2 (b), 3.1 CH_2 (c), 7.5 triplet NH_3 (d) and 4.7 DOH (f).

Preparation of working electrodes

The iron mould with cooling system and temperature control unit the same as the grid casting machine of Sovema Co. (Verona, Italy) was used for preparing the working electrode. The working electrode, a wire with a geometric area of 0.50 cm^2 with Pb– 1.66% Sb– 0.24% Sn composition, was prepared and was enveloped with an epoxy resin.

The carbon–lead oxide paste electrode was prepared via mixing $50:50\%$ (*w/w*) graphite with lead oxide powder [7], washed with diethyl ether and dried under vacuum, which was then mixed with the appropriate amount of mineral oil with thorough hand mixing in a mortar and pestle. The paste was then packed into the end of a glass tube (approx. 2-mm i.d., 10 cm long) equipped with a copper wire serving as an external electric contact. Before every measurement, the fresh surfaces were obtained by polishing the electrode on a clean paper.

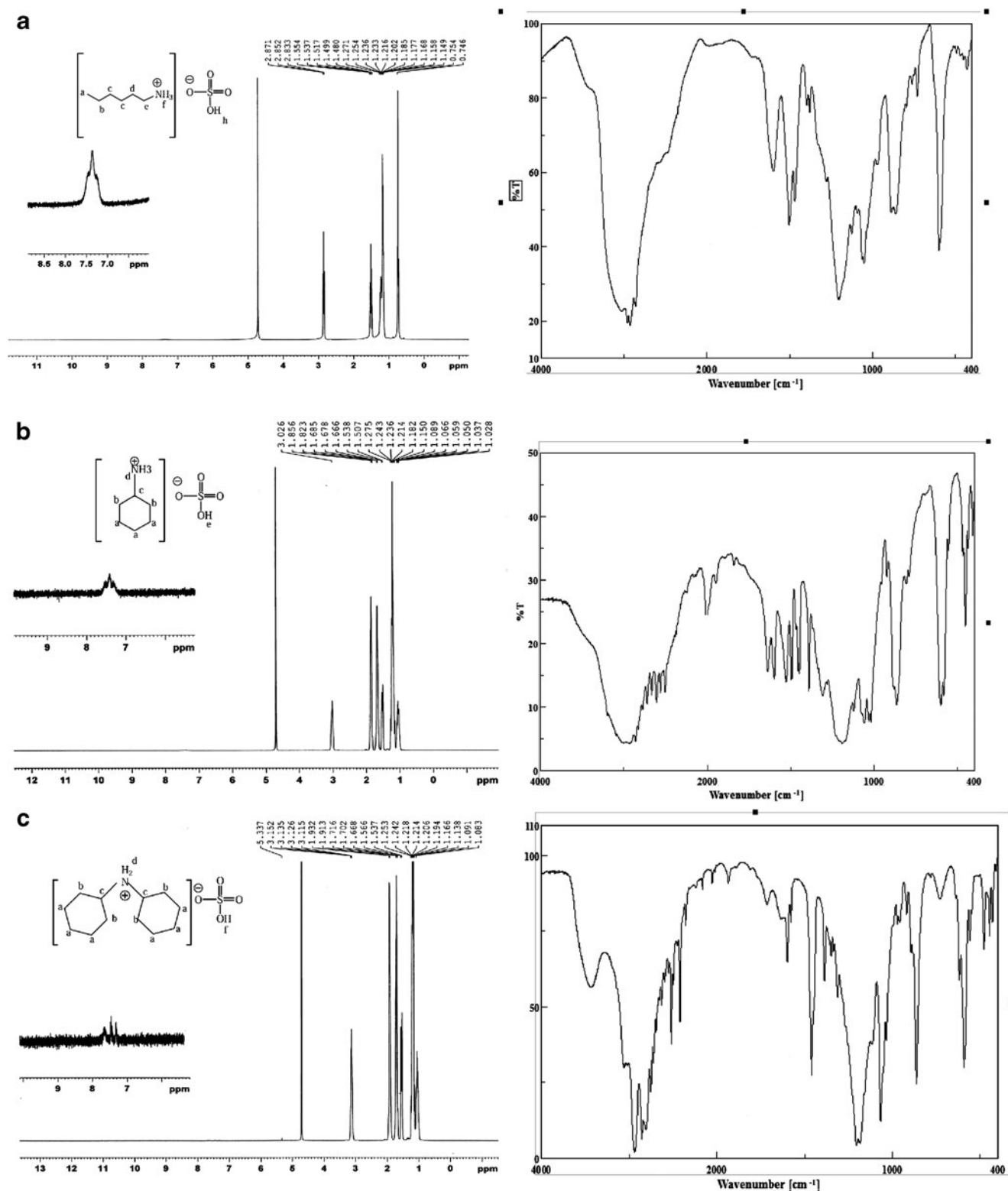


Fig. 1 ¹H NMR (400 MHz, D₂O) and IR (KBr) spectra of HAHS (a), MCHAHS (b) and BCHAHS (c)

Procedure

In this study, most experiments were carried out with Pb–1.66% Sb–Sn alloy because in maintenance-free batteries,

the grids are made with low antimony alloy (1–2 wt.%). Prior to each experiment, the lead alloy electrode was mechanically polished with a water-resistant emery paper (P 1000), thoroughly rinsed with doubly distilled water in

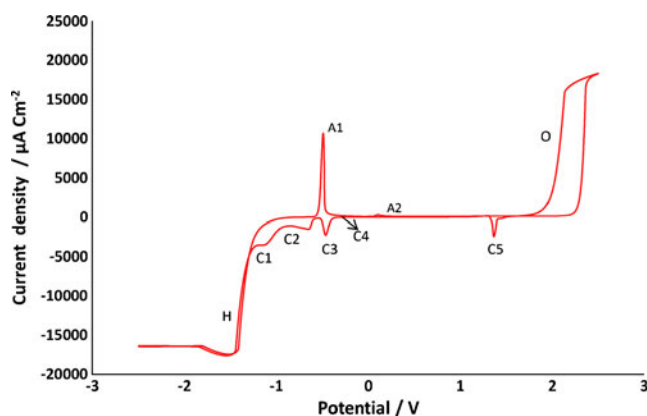


Fig. 2 Cyclic voltammogram of Pb–1.6% Sb–0.24% Sn alloy at the scan rate of 50 mV s^{-1} in $4.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$

order to remove oxides, and sulphates formed on the surface of the electrode. Cyclic voltammograms of lead alloy electrodes in the sulphuric acid solutions with and without IL in the potential region between hydrogen and oxygen evolution (-2.50 to $+2.50 \text{ V}$ vs. SCE) were obtained at a sweep rate of 50.0 mV s^{-1} .

Linear sweep voltammograms (LSV) was used to study the effect of various ILs on the hydrogen and oxygen

evolution of lead alloy electrodes in sulphuric acid solutions. The sweep rate was 50.0 mV s^{-1} .

The cyclic voltammograms (CV) of carbon–lead oxide paste electrodes were obtained at the sweep rate 50.0 mV s^{-1} , in the potential range from -0.10 to 0.80 V vs. SCE. All experiments were carried out at room temperature (298 K).

Result and discussion

The CV voltammogram of lead–1.6% antimony electrode in sulphuric acid solution, 4.0 mol dm^{-3} , at the potential region between hydrogen and oxygen evolution (from -2.50 to $+2.50 \text{ V}$ vs. SCE), is shown in Fig. 2.

Peaks H and O are assigned to the reduction of hydrogen ions and oxidation of water that led to hydrogen and oxygen evolution. In the anodic potential sweep of the voltammogram, peak A_1 corresponds to the formation of lead sulphate [21–24], and peak A_2 at the potential of about 0.00 V is related to the oxidation of antimony [25]. In the cathodic potential sweep, five current peaks appear, corresponding to the transitions of PbO_2 to PbSO_4 (C_5). The small reduction of the current peak at a potential of

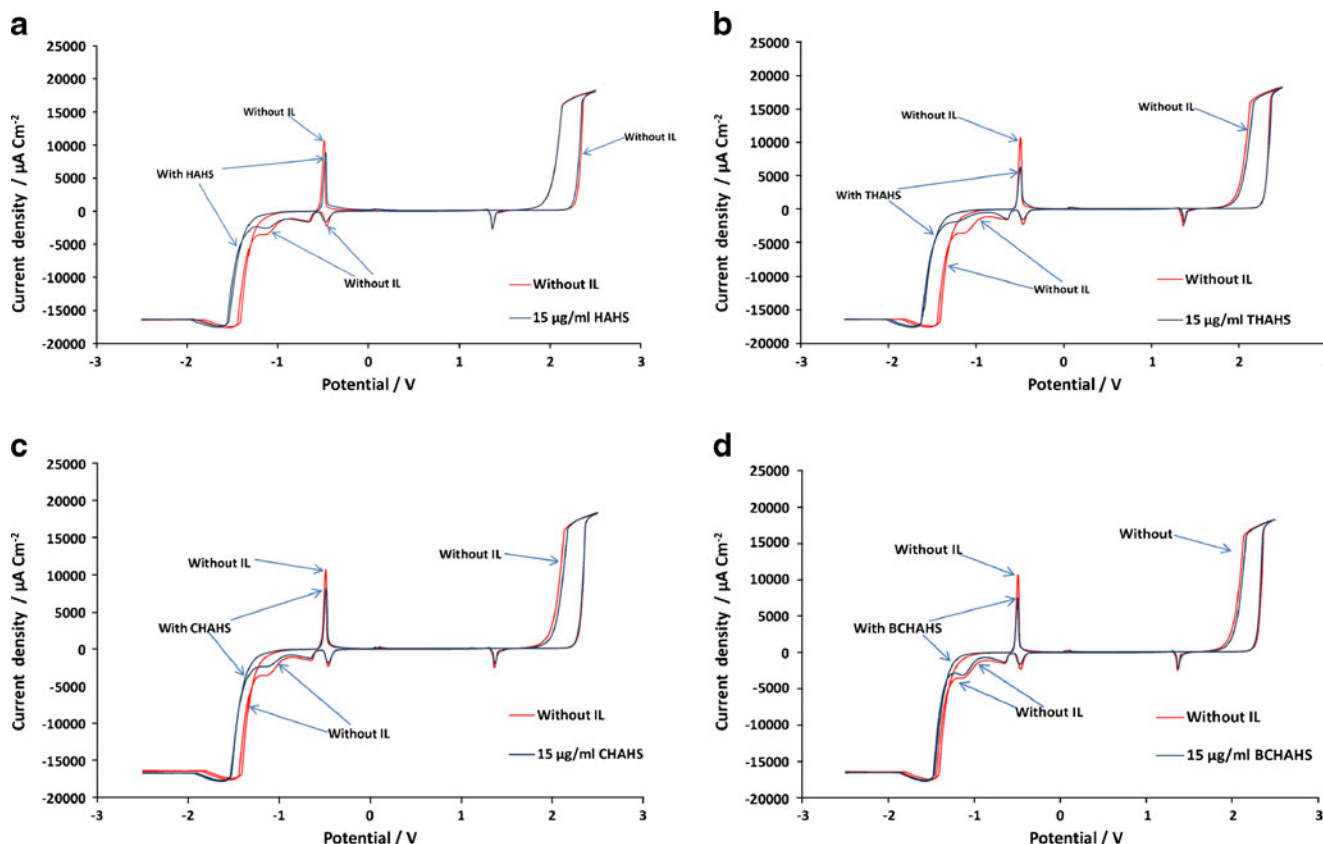


Fig. 3 Cyclic voltammograms of Pb–1.6% Sb–Sn alloy electrode in 4.0 mol dm^{-3} sulphuric acid solution with and without 15.0 μg ml^{-1} IL at the sweep rate of 50.0 mV s^{-1}

about -0.25 V is related to the reduction of antimony (C_4), and the other peaks correspond to the reduction of PbO to Pb (C_3) and $PbSO_4$ to Pb (C_1 , C_2) [7, 20–24].

Two reduction peaks of $PbSO_4$ appear on the negative-going potential sweep curves (C_1 and C_2) assigned to the reduction of large and small $PbSO_4$ crystals, respectively. In charge/discharge cycles, many small $PbSO_4$ crystals are formed over big crystals, which are very difficult to be reduced [26]. Therefore, the electrode surface is covered by many small $PbSO_4$ crystals. This anodic layer is formed in the region between -0.52 and 0.00 V vs. SCE passivated on the electrode surface. The wide current plateau above 0.00 (V), where the current is independent of the potential, corresponds to the potential region in which lead oxide formation occurs, with the (+2) oxidation state of lead. Since the PbO layer is in a direct contact with the electrode, its reduction is possible, which results in the current peak C_3 in the cathodic portion of the voltammogram. The results of some investigations indicate that lead oxidation to PbO or basic sulphates under the $PbSO_4$ membrane begins at the potential of -0.20 V vs. SCE [27, 28]. The initial reaction of sulphuric acid with lead oxide leads to the formation of normal lead sulphate and heat evolution. Normal lead sulphate is not stable under the influence of excess lead oxide and water and converts into basic lead sulphate, either tribasic lead sulphate ($3PbO \cdot PbSO_4$) or tetrabasic lead sulphate ($4PbO \cdot PbSO_4$). Tribasic lead sulphate is crystallized as small needles with high specific surface; however, tetrabasic lead sulphate forms more bulky crystals.

Oxygen evolution overpotential

Figure 3a–d shows the CVs of lead–1.6% antimony electrode in the sulphuric acid solution with and without different ILs in the potential range between hydrogen and oxygen evolution obtained at the sweep rate of 50.0 $mV\ s^{-1}$. It is found that the number of chain and structure (linear and cyclic) of ILs have valuable effects in the electrochemical performance of lead acid battery grids at the same concentration.

Oxygen oxidation and reverse oxygen oxidation potential were obtained respectively at potentials of 2.31 and 2.02 V from LSV and compared as a function of IL concentration. Figure 4a indicates that unlike other ILs, THAHS increases, the oxygen oxidation overpotential. Also, the reverse oxygen oxidation potential depends slightly on the IL concentration. The obtained results show that with increasing the number of linear alkyl chains in alkylammonium cation, oxygen oxidation overpotential increases, whilst the increase in the number of cycloalkyl chains in cycloalkyl ammonium cation decreases the oxygen oxidation overpotential. Also, Fig. 4b shows that

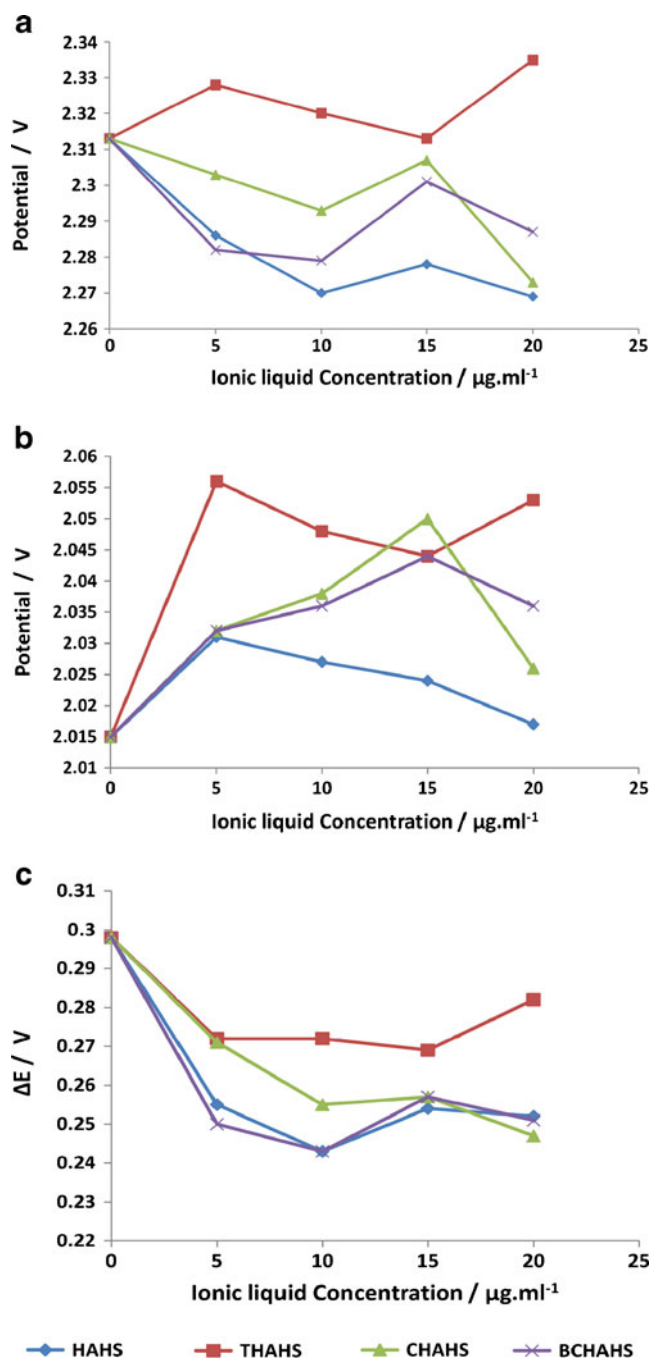
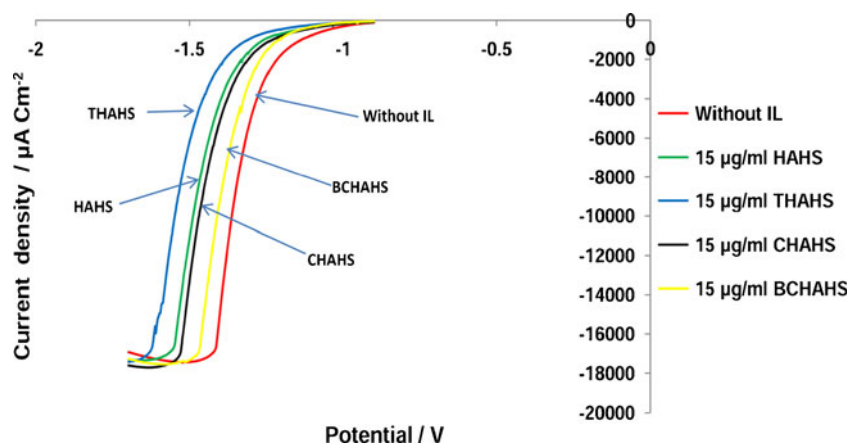


Fig. 4 Oxygen oxidation potential at a scan rate of 50.0 $mV\ s^{-1}$ in 4.0 $mol\ dm^{-3}$ H_2SO_4 in various concentrations of ILs with current density of 4.0 $mA\ cm^{-2}$ at the anodic scan (a), cathodic scan (b) and differences of oxygen oxidation potential between anodic and cathodic scans (ΔE) (c)

all ILs increase the reverse oxygen oxidation overpotential. The reverse oxygen oxidation overpotential increases with increasing the number of linear alkyl chains in alkylammonium cation, but the reverse oxygen oxidation overpotential decreases with increasing the number of cycloalkyl chains in cycloalkyl ammonium cation.

Fig. 5 Linear sweep voltammograms of Pb–1.6%Sb–Sn alloy in various ILs and the same concentration of $15.0 \mu\text{g ml}^{-1}$, scan rate 50.0 mV s^{-1} and $4.0 \text{ M H}_2\text{SO}_4$



Finally, Fig. 4c shows the influence of ILs on the differences of oxygen oxidation potential between anodic and cathodic scans (ΔE). The results show that ΔE decreases in the presence of different ILs. Also, increasing the number of linear alkyl chains in alkylammonium cation increases the ΔE , whilst increasing the number of cycloalkyl adding chains in cycloalkyl ammonium cation results in the decrease of ΔE .

Hydrogen evolution overpotential

Figure 5 shows the LSV of hydrogen gas evolution of Pb–1.6%Sb–Sn alloy in the presence of various ILs in the same concentrations ($15 \mu\text{g cm}^{-3}$) and 4.0 mol dm^{-3} sulphuric acid electrolytes. As can be seen in this figure, in the presence of all four ionic liquids, hydrogen evolution potential shifts to more negative values. Among them, THAHS has the most significant effect on hydrogen overpotential. Also, Fig. 6 illustrates that with increasing the number of alkyl chains in alkylammonium cation, hydrogen overpotential has become more negative, but with increasing the number of cycloalkyl chains in cycloalkyl

ammonium cation, hydrogen overpotential has become more positive. The important point, which is obtained from the results, is that the increase in hydrogen overpotential has a linear correlation with the number of alkyl chain in alkylammonium cations, i.e. tetra-HAHS with long alkyl groups is the most effective ionic liquid which can considerably impede the hydrogen gas evolution and, hence, water loss.

Formation and reduction of oxide layer on Pb–Sb electrode surface

Figure 3a–d shows that the different IL additives in electrolyte have the same effect on the oxidation current of Pb to PbSO_4 (peak A_1); also, the current corresponding to lead sulphate formation decreases with the addition of different ILs or by increasing their concentration (Fig. 7). Figure 8a shows a decrease in C_1 peak currents for all ILs, related to the reduction of large PbSO_4 crystals [7], which decreases with the increase in IL concentration. A comparison between Figs. 6 and 8a shows an inverse relation between hydrogen overpotential and the amount of β - PbSO_4 formed on the surface of electrodes. The results demonstrate that with the increases in the number of alkyl chains in alkylammonium cation, the cathodic peak current of changing β - PbO_4 to Pb decreases, whilst increasing the number of cycloalkyl chains in cycloalkyl ammonium cation has an inverse effect.

Figure 8b exposes the effect of ILs on the conversion reaction of PbO to Pb. All ILs reduce the amount of conversion in low concentrations, but in higher concentrations, this behaviour does not depend on the IL concentration.

Positive and negative active materials

During the discharge/charge processes in lead acid batteries, Pb in negative electrode and PbO_2 in positive electrode change to Pb (II), and vice versa [29]. The electrochemical

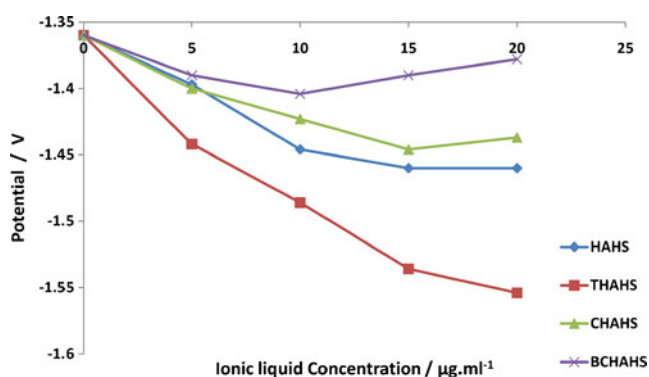


Fig. 6 Effect of different ILs and their concentrations on the hydrogen evolution overpotential of Pb–1.6%Sb–Sn alloy in $4.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, scan rate 50.0 mV s^{-1} and current density of 8.0 mA cm^{-2} for the cathodic scan

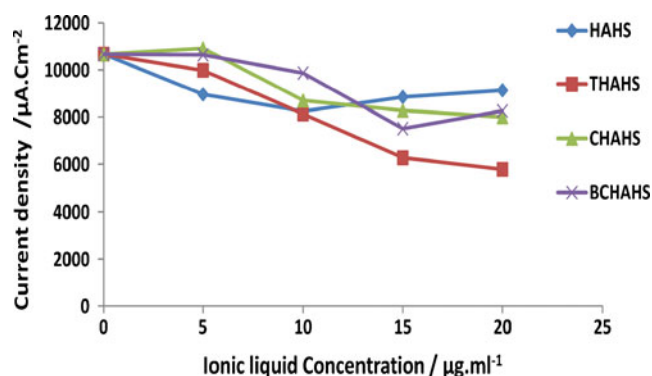


Fig. 7 Effect of different ILs and their concentrations on the current density of conversion of Pb to PbSO₄ at the sweep rate 50.0 mV s⁻¹ in 4.0 mol dm⁻³ H₂SO₄

effects of ILs in the conversion of PbSO₄ to PbO₂ and vice versa were investigated by carbon–PbO electrode. PbO in H₂SO₄ solution reacts immediately with acid, forming lead sulphate and basic lead sulphates (tribasic or tetrabasic). As shown in Fig. 9, in the presence of BCHAHS and THAHS in different concentrations, the conversion current of PbSO₄ to PbO₂ (I_a and I_c) increases, whilst the reversibility, deduced from peak potential differences, decreases. Other ILs have shown similar behaviours. Interaction between Pb²⁺ and ILs makes the more stable species of Pb²⁺ [7]. During PbSO₄ formation, IL cations are transferred from solution on the surface of electrode and adsorbed on the surface by physical and electrical interactions. This behaviour is observed using multicycle CV because ILs are stable. Therefore, different behaviours observed for each ILs, due to its size and charge density, are dependent on the different structures and numbers of chain of cations in these ILs.

Therefore, more PbSO₄ are formed, leading to an increase in PbSO₄ to PbO₂ conversion current, which is a beneficial effect in negative and positive active materials in the battery.

Conclusion

The influence of various types of alkylammonium hydrogen sulphate differing in the number of alkyl and cycloalkyl chains on the electrochemical behaviour of a lead antimony electrode in sulphuric acid was investigated using CV methods. The obtained results show that in the presence of all studied ionic liquids, fewer PbSO₄ crystals are formed on the electrode surface. Morphological changes of the PbSO₄ layer play an important role in dictating the electrochemical reactions of lead alloy. Previous studies demonstrated that each form (such as thribasic or tetrabasic and α -PbSO₄ or β -PbSO₄) produces different current

densities in the lead acid batteries at the same conditions. Also, different crystal structures of PbSO₄ have unlike effects on the hydrogen and oxygen evaluation. According to the results in Figs. 3, 4, 5, 6, 7, 8 and 9, we can say that with the increase of cation chains in alkyl ammonium hydrogen sulphate, β -PbSO₄ formation on the grid surface decreased more compared with cycloalkyl chains. Therefore, by increasing chains in cycloalkyl cation, it can be found that the current density of PbSO₄ production is increased. Also, all studied ILs increased the hydrogen evolution overpotential.

Investigation on a family of alkylammonium hydrogen sulphate ionic liquids shows that the electrochemical behaviours of lead alloy are mainly under the influence of the number of alkyl and cycloalkyl chains in alkylammonium cations. Hydrogen evolution potential has a reversed linear correlation with the number of alkyl and cycloalkyl chains. The results show that the electrochemical behaviour of lead antimony alloy depends on the number and the structure of organic groups on the ionic liquids cations and the concentration of ILs. Hence, all ILs reduce the current density of the conversion of Pb to PbSO₄ and PbO to Pb. Also, the cyclic voltammogram of PbO–carbon paste electrode shows that increasing the concentration of ionic liquids increases the conversion current of PbSO₄ to PbO₂

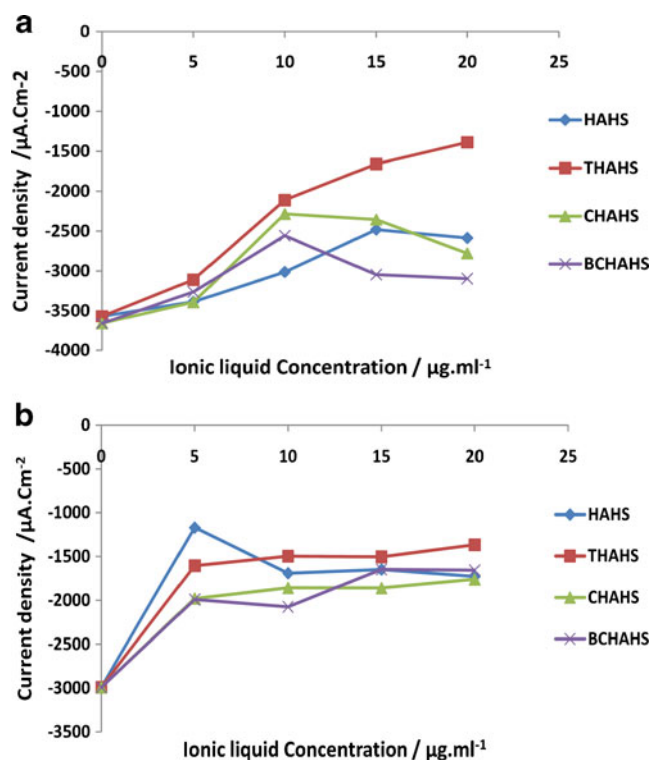
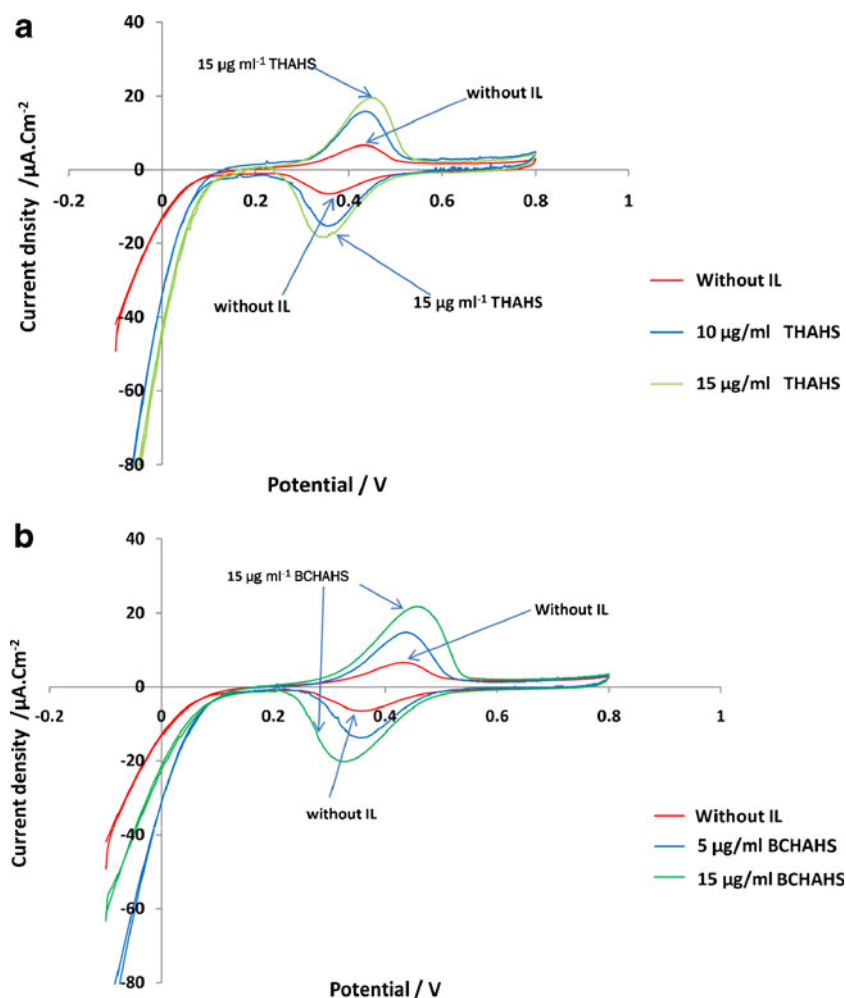


Fig. 8 Effect of different ILs and their concentrations on the current density of conversion of β -PbSO₄ to Pb (a) and PbO to Pb (b) for Pb–Sb–Sn alloy at the scan rate of 50.0 mV s⁻¹ and 4.0 M H₂SO₄ in the cathodic scan

Fig. 9 Cyclic voltammograms (anodic and cathodic current) of PbSO_4 to PbO_2 in the presence of different concentrations of BCHAHS (a) and THAHS (b) at the modified PbO -carbon past electrode, scan rate 50.0 mV s^{-1} and $4.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$



whilst decreasing the reversibility. Also, the results show that using the ILs in a very low concentration ($5\text{--}20 \text{ µg ml}^{-1}$) can improve the electrochemical performance of lead acid batteries.

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